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⑤④ **Thermoformable laminate structure.**

⑤⑦ Thermoformable laminate structure comprising foamed thermoplastic sheet having a cloth adhesively bonded to one surface thereof. The cloth is impregnated with a polymer having a softening temperature greater than 75°C.

EP 0 146 519 A2

THERMOFORMABLE LAMINATE STRUCTURE

This invention relates to thermoplastic materials, and particularly to a thermoformable laminate structure comprising foamed thermoplastic sheet which may be molded into complex shapes. More particularly this invention relates to a method for fabricating a thermoformable laminate structure having a fabric coating which is adhered with a polymer which has a high softening temperature and to such structure.

DESCRIPTION OF THE PRIOR ART

Foamed thermoplastic laminates have been used for many years. These laminates were most often formed as a sandwich structure in which the foamed thermoplastic material was enclosed between liner board facings. An example of this construction is a polystyrene foam sheet which has a kraft paper liner board facing on each side. Such laminate has been formed by die-cutting or scoring and by pressing the board and applying a resin to fix the pressed shape. However, the kraft paper liner board facing is a material which is not easily molded and which has a tendency to wrinkle during any molding of the laminate structure.

Other efforts have been made to provide a laminate structure which may more easily be molded. A thermoplastic laminate has been formed of a layer of foamed styrene-maleic anhydride polymer to which a thermoplastic polymer skin is bonded. This laminate is moldable without the problems caused by the earlier developed paper facings.

More recent efforts have provided moisture-resistant, moldable thermoformable laminate structures formed from foamed thermoplastic sheet which are faced by a polymer impregnated cloth. For instance the cloth can be impregnated with an acrylic polymer having a high softening temperature.

Such laminate structures have been formed, for instance, by soaking the cloth in a solution of polymer to impregnate the cloth with the solution of polymer. The solvent is allowed to evaporate to provide a cloth impregnated with the polymer. Laminates have been formed by bonding such cloth impregnated with polymer to a sheet of thermoplastic foam.

Such laminate forming procedure is not without disadvantages. For instance an inordinate amount of polymer is utilized on a unit area basis in making such laminate structures. Also excessive time is required to allow for solvent evaporation from the cloth impregnated with polymer solution.

The process of the invention provides a thermoformable laminate structure having polymer impregnated cloth adhered to at least one side of a sheet of thermoplastic foam, without the disadvantages of prior art processes.

SUMMARY OF THE INVENTION

This invention provides a thermoformable laminate structure comprising a foamed thermoplastic sheet having adhered to one side a polymer-impregnated cloth. Desirably the cloth comprises synthetic fibers and readily elongates in any direction in its surface. The cloth is impregnated with a polymer which has a softening temperature greater than 75°C.

This invention also provides a process comprising applying a polymer emulsion film to a

surface of a sheet of thermoplastic foam; allowing the emulsion film to dry by evaporation of liquids; applying a cloth to the dry emulsion film; impregnating the cloth with the polymer of the film by
5 applying heat and pressure to the surface of the cloth; and adhering the cloth to the sheet of thermoplastic foam by removing said heat and pressure from the surface of the cloth, allowing the polymer to cool and solidify. Alternatively the
10 cloth can be applied to the wet emulsion film. By applying heat and pressure, moisture is driven off while the cloth is laminated to the thermoplastic foam.

A further process provided by this invention
15 comprises applying a polymer emulsion film to a surface of a sheet of thermoplastic foam; applying a cloth to the emulsion film and allowing the polymer to impregnate the cloth; allowing the emulsion to dry by evaporation of liquids; adhering the cloth to the
20 sheet by applying heat and pressure whereby the emulsion solids become plastic and removing the heat and pressure to allow the polymer to cool and solidify.

In yet another process of this invention a cloth impregnated with a polymer can be bonded
25 to the sheet of thermoplastic foam.

DESCRIPTION OF PREFERRED EMBODIMENTS

The thermoformable laminate of this invention comprising a foamed thermoplastic sheet having adhered to one side a polymer-impregnated cloth is preferably
30 fabricated utilizing a polymer having a softening temperature of at least 75°C.

The foamed thermoplastic sheet can comprise a variety of foamable thermoplastic materials for instance polystyrene, styrene copolymers such as
35 styrene-maleic anhydride polymer and styrene-acrylonitrile polymer, and the like. Foamed thermoplastic sheets may also comprise other foamed thermoplastic

material which would be substantially rigid at moderate temperatures for instance polyolefins such as polyethylene. However, adhesion to polyethylene is generally difficult without surface treatment such as flame treating. The preferred material for providing the foamed thermoplastic sheet useful in the process of this invention comprises polystyrene and is thermoformable at temperatures up to about 180°C.

The foamed thermoplastic sheet can be provided in any thickness desired. Foamed thermoplastic sheet which is particularly useful in the laminate of this invention will generally be less than 30 millimeters in thickness. The preferred thickness of the foamed thermoplastic sheet for use in fabricating composite laminates will generally be between 2 millimeters and 20 millimeters.

The thermoformable laminate of this invention has a polymer-impregnated cloth adhered to one side of the foamed thermoplastic sheet. The process of this invention provides a polymer-impregnated cloth adhered to at least one side of the foamed thermoplastic sheet. The polymer-impregnated cloth provides stability to the laminate, for instance a composite laminate, which has been thermoformed into a complex shape at thermoforming temperatures in the range of 130°C. to 180°C. Such thermoforming temperature range is limited at the lower temperature of 130°C., the temperature at which the foamed thermoplastic sheet is readily thermoformable. This range is limited at the higher temperature by the degradation (i.e., foam collapse) temperature of the material of the foamed thermoplastic sheet. Accordingly, the upper level of the thermoforming temperature range depends on the foamed thermoplastic material utilized. Temperatures of up to about 180°C. are satisfactory for molding laminates using foam comprising styrene-maleic anhydride copolymers. However the upper temperature limit

for thermoforming laminates using foam consisting of polystyrene is about 150°C.

For purposes of this invention the term "softening temperature" is intended to mean softening point as determined by thermomechanical analysis using a program designated "TADS TMS STD TEVO1.04 PCN 05.06B01.01.04" provided by Perkin Elmer using a Perkin Elmer Model TMS2, Thermomechanical Analyzer. Analytical parameters were: probe load: 10 grams; minimum temperature: 25°C.; maximum temperature: 200°C.; heating rate: 5°C. per minute; cooling rate: 20°C. per minute; penetration probe: round tip. Polymer samples were approximately 1/4 inch x 1/8 inch x 1/16 inch (6.35mm x 3.18mm x 1.6mm). Thermomechanical analysis comprises placing a weighted compression probe on a thin sample which is slowly heated at a uniform rate. The temperature at which the probe begins to penetrate the sample is the softening point which is determined by the intersection of tangent lines about the inflection point on the plot of penetration distance versus temperature near the temperature at which the probe begins to penetrate the sample. Polymers useful in the laminate structure of this invention will have a softening temperature greater than 75°C, but lower than the minimum thermoforming temperature of other material, e.g. about 130°C or up to about 180°C.

The cloth can comprise a variety of textile structures for instance the cloth may be woven or non-woven. A desired characteristic of the cloth is that it elongates sufficiently in a direction in its surface to conform to the desired complex shape to be imparted by the thermoforming process. Desirable cloth will comprise a fabric that can elongate, for instance in the range of about 10-50 percent, at

thermoforming temperature without destroying integrity of the fabric structure. Since woven cloths of natural or glass fibers generally exhibit elongation of less than 10 percent, they are not useful in providing moldable, thermoformable laminates. Preferred cloth which can undergo such elongation comprises non-woven fabric such as non-woven spun-bonded polyester fabric. Other cloths which may be useful include non-woven polyester, non-woven nylon and non-woven polypropylene. The cloth can have any thickness which may be desired. Typically useful cloth will have a thickness in the range of 0.05 to 1.0 millimeters. However, cloth having a larger thickness may be used. Preferably the cloth will be non-woven and will have a thickness of from 0.1 to 0.4 millimeters. Typically useful cloth will also have a basis weight in the range of 0.3 to 10.0 ounces per square yard (10-340 grams per square meter), preferably in the range of 1.0 to 6.0 ounces per square yard (34-203 grams per square meter).

PROCESS OF THIS INVENTION

The polymer-impregnated cloth can be prepared by soaking the cloth in a solution of polymer and solvent, for instance cloth can be pulled through a vat of a solution and then through a set of rolls to remove excess solution. The cloth can be dried to remove excess solvent and then adhered to one side of the foamed thermoplastic sheet. The adhesion can be effected by any adhesive that will bond the polymer-impregnated cloth to the foamed thermoplastic sheet. Preferably the adhesive will not exhibit creep at low temperatures for instance below the softening temperature of the foam. Acrylic adhesives are useful for this purpose.

Desirable soluble polymers include those polymers which are designated in commerce as resins. Polymers that are soluble in liquids such as water and lower alcohols such as methanol, ethanol, N-propanol, etc. are preferred. The most preferred polymers are those which are soluble in water, for instance solutions of water and ammonia. Such resins include acrylic resins, such as styrene-methacrylic acid copolymers. One such acrylic resin which is soluble in a water-ammonia solution is available from S. C. Johnson & Son, Inc. as Joncryl 678 acrylic resin, which has a softening temperature of 89°C.

Other resins such as a phenolic resin may also be used. When a phenolic resin is used instead of the preferred acrylic resin the fabrication process must be modified to prevent a complete cure of the phenolic resin before the laminate structure is molded into the desired final shape. When the phenolic resin is completely cured it is no longer moldable; thus, during the preparation of the laminate structure, the phenolic resin impregnated fabric must be only partially cured. It must remain partially cured until the final molding step. The use of an acrylic resin, which is preferred, eliminates the handling problems such as storage to prevent curing and emission of volatile materials which are associated with the use of a phenolic resin. The coating is bonded to one of the surfaces of the layer of foamed thermoplastic material. This may be accomplished by heat treatment during the laminating or by an adhesive which is preferably water dispersed.

Such acrylic resins must also of course exhibit a softening temperature greater than about 75°C. Such high softening temperature allows for a stable laminate especially for uses where local temperatures may become moderately high.

Polymer emulsions are also particularly useful in the process of this invention and comprise particles of polymer dispersed in a vehicle, for instance comprising water. Preferred emulsions can contain up to about 50 percent by weight of solid polymer particles. Alternatively, the emulsion can comprise higher amounts of solid polymer particles say up to 80 percent by weight. Preferred polymer comprises acrylic polymer. Such polymer has a softening temperature greater than 75°C., but lower than the minimum thermoforming temperature of foamed thermoplastic sheet, for instance about 130°C. or up to about 180°C.

The process of this invention utilizing a polymer emulsion film to fabricate cloth faced foam laminates is generally more economical than other methods in that substantially lower quantities of polymer are required to form a laminate. For instance, it has been found that less than 16 grams (for instance, from about 5 to 8 grams) polymer is required per square meter of laminate by this process using polymer emulsion film. On the other hand it has been generally found that about 40 grams of polymer are utilized per square meter of laminate in those processes where the cloth is soaked in a polymer solution before application to the foam sheet.

The cloth can be laid over the wet polymer emulsion film. The composite of cloth, polymer emulsion film and foamed thermoplastic sheet can then be optionally calendared to promote penetration of the polymer emulsion film into the cloth. The laminate can be formed by allowing the solvent to evaporate from the polymer emulsion at the outer surface of the cloth.

Alternatively the polymer emulsion film overlaying a surface of the foamed thermoplastic sheet can be allowed to dry prior to application of the cloth. The cloth can be applied to the dry film and

the laminate formed by the application of heat and pressure. For instance, a hot surface having a temperature of about 120 to 150°C can be pressed on the cloth to cause the polymer film to penetrate into and impregnate the cloth.

A suitable polymer emulsion may contain an adhesive to promote adhesion of the polymer emulsion film to the foamed thermoplastic sheet. Such adhesive can comprise an acrylic adhesive such as is available from Rohm and Haas as E2138 acrylic adhesive or E1958 acrylic adhesive. Such adhesive can be mixed, for instance, in equal weight proportions, with the acrylic emulsion, such is available from S. C. Johnson & Son, Inc. as Joncryl 89 styrenated acrylic dispersion, a water based emulsion of about 48 percent by weight acrylic solids, having a softening temperature of 101°C.

The following examples illustrate certain embodiments of laminate structures and processes in accordance with this invention.

EXAMPLE I

This example illustrates the forming of a moldable, thermoformable laminate structure of this invention according to a process of this invention.

A mixture of polymer emulsion was prepared by combining equal weights of two aqueous acrylic emulsions.

The first aqueous acrylic emulsion was identified as Joncryl™ 89 styrenated acrylic dispersion (available from S.C. Johnson & Son, Inc., Johnson Wax Chemical Products Division) which comprises 48 ± 1 percent by weight solids in water at a pH in the range of 8.0 to 8.5. The emulsion has a milky appearance, a viscosity in the range of 400 to 600 centipoises and a density of 8.7 pounds per gallon (1.04 g/cm³).

The second aqueous acrylic emulsion was identified as adhesive E-2138 (available from Rohm and Haas Company) which comprises 51 to 53 percent by

weight acrylic polymer in water at a pH in the range of 8.2 to 8.6. The emulsion has a milky-blue color, a mild ammoniacal odor due to about 25 ppm of ammonia, and contains about 0.5 ppm of formaldehyde. The emulsion has a viscosity in the range of 40,000 to 50,000 centipoises.

The mixture of the two acrylic polymer emulsions was applied in a thin film to one surface of a sheet of polystyrene foam having a thickness of about 130 mils (3.3 mm) and a density of about 42 pounds per thousand square feet (205 grams per square meter). The film was applied at a thickness of about 0.75 mil (19×10^{-6} m) with a No. 8 stainless steel metering rod comprising No. 8 wire (having a diameter of 0.162 inches (4.1 mm)) wound on a rod having a diameter of 1/2 inch (about 13 mm). The emulsion film was applied at about 1.5 pounds per thousand square feet (7 gm/m^2).

While the film was still wet, a piece of spun-bonded, non-woven polyester fabric was laid onto the emulsion coated surface of the polystyrene foam. The polyester fabric had a basis weight of 1.0 ounces per square yard (33.9 gm/m^2) and is identified as Reemay 2014 by duPont.

The fabric was then laminated to the polystyrene foam in a Wabash Hydraulic Press, Model 50-2424-2 STMA, by Wabash Metal Products, Inc., having steam heated plates set for a temperature of 260°F. (127°C.). The press was equipped with shims which provided a forming cavity in which the foam was allowed to expand. The wet laminate was heated within the press for 30 seconds, after which the press was cooled for about 90 seconds to a temperature of about 100°F. (38°C.). The laminate sheet then had a thickness of about 150 mils (3.8 mm).

5 The polyester fabric was laminated to the polystyrene foam with good adhesion. Adhesion can be determined by pulling the fabric to effect delamination. If fibers from the non-woven fabric separate from the fabric and are left adhered to the foam, adhesion is considered excellent. If there is delamination with no fibers left on the foam, adhesion is considered good.

EXAMPLES II-V

10 The lamination procedure of Example I was repeated using a variety of non-woven fabrics.

II. Fabric: non-woven polypropylene having a basis weight of 68 gm/m².

Adhesion: good.

15 III. Fabric: non-woven polypropylene having a basis weight of 105 gm/m².

Adhesion: good.

IV. Fabric: non-woven polyester having a basis weight of 163 gm/m².

20 Adhesion: excellent.

V. Fabric: non-woven polyester having a basis weight of 197 gm/m².

Adhesion: excellent.

25 Although adhesion is only good in the laminate of Examples II and III, such laminates would be acceptable and suitable for less severe applications.

EXAMPLE VI

30 This example illustrates the thermoformability of the laminate structures of this invention as prepared in Example 1.

The laminate structure prepared in Example 1 was thermoformed in a Comet thermoformer, Labmaster Model 14x20, by Comet Industries, Inc. The three-dimensional mold was of a design representing a seat buckle cover as used in some General Motors automobiles. The thermoformer operates by carrying the flat laminate

sheet into an infrared heater section to preheat the flat laminate sheet to a softening temperature for the material of the sheet so that the sheet can be readily formed. The sheet was in the heater section for 8
5 seconds where it reached a temperature in the range of 260 to 290°F. (127-143°C.). The heated sheet was then moved into the open mold block which was heated to 70°F. (21°C.). The cooled molded laminate had good three-dimensional definition with no signs of de-
10 lamination and no wrinkles.

EXAMPLES VII-X

The thermoforming procedure of Example VI was repeated using the laminate structures prepared in Examples II-V.

15 VII. Thermoforming of the laminate sheet prepared in Example II. The cooled molded laminate had good three-dimensional definition, but the polypropylene fabric partially delaminated from the
20 polystyrene foam.

VIII. Thermoforming of the laminate sheet prepared in Example III. The cooled molded laminate had good three-dimensional definition, but the polypropylene
25 fabric partially delaminated from the polystyrene foam.

IX. Thermoforming of the laminate sheet prepared in Example IV. The cooled molded laminate had good three-
30 dimensional definition with no signs of delamination and no wrinkles.

X. Thermoforming of the laminate sheet prepared in Example V. The cooled molded laminate had good three-
35 dimensional definition with no signs of delamination and no wrinkles.

Although there was some delamination and wrinkles in the laminates thermoformed in Examples VII and VIII, such laminates comprising polypropylene fabric would be suitable for applications requiring less severe thermoforming, for instance, such as automobile headliners where the thermoforming mold would not draw as deeply or at sharp angles.

EXAMPLE XI

This example illustrates an alternative method of producing the thermoformable laminate structure of this invention.

A bath of acrylic polymer solution was prepared using Joncryl™ 61LV acrylic resin solution (available from S. C. Johnson & Son, Inc.) which has the following formulation:

acrylic resin	35.0 weight percent
28% aqueous ammonia	7.5 weight percent
ethylene glycol	1.5 weight percent
isopropyl alcohol	5.0 weight percent
water	51.0 weight percent

The acrylic resin component had a softening temperature of 85°C.

The acrylic polymer solution was diluted with water to an acrylic resin level of 27 percent by weight.

A cloth sheet of spunbonded non-woven polyester fabric was soaked in the bath to impregnate the fabric with the acrylic polymer solution. Excess solution was removed by passing the fabric through a pair of rubber-coated squeeze rolls. The cloth was then placed in an oven at 180°F. (82°C.) for five minutes to remove liquids providing a dried polymer impregnated cloth, which comprised about 50 percent by weight acrylic polymer.

A sheet of polystyrene foam having a thickness of about 130 mils (3.3 mm) and a density of about 42 pounds per thousand square feet (205 grams per square

meter) was coated on one surface with an aqueous acrylic emulsion identified as adhesive E-1958 (available from Rohm and Haas Company) which comprises 57 to 59 percent by weight acrylic polymer in water at a pH in the range of 4.0 to 5.0. The emulsion has a milky-white color, a mild acrylic odor. The emulsion has a Brookfield viscosity in the range of 2,000 to 4,000 centipoises. A catalyst solution of 15 percent by weight of sesquicarbonate (equimolar amounts of sodium bicarbonate and sodium carbonate) was added to the emulsion at a level of 4 parts per 100 parts of the emulsion. The catalyzed emulsion was applied to the surface of the polystyrene foam with a No. 8 stainless steel metering rod comprising No. 8 wire (having a diameter of 0.162 inches (4.1 mm)) wound on a rod having a diameter of 1.2 inch (13 mm) and allowed to dry.

The dried polymer impregnated cloth was applied to the surface of polystyrene foam coated with dried acrylic emulsion. Lamination was effected in a Wabash Hydraulic Press, Model 50-2424-2 STMA, by Metal Products, Inc. The press had steam heated plates at a temperature of 260°F. (127°C.) which were spaced apart by shims to provide a forming cavity in which the polystyrene foam was allowed to expand. The laminate was heated within the press for 30 seconds, after which the press was cooled for about 90 seconds to a temperature of about 100°F. (38°C.). The dry laminate structure then had a thickness of about 150 mils (3.8 mm).

EXAMPLE XII

The thermoforming procedure of Example VI repeated using the laminate structure prepared in Example XI. The cooled molded laminate had good three-dimensional definition with no wrinkles.

USES OF THE THERMOFORMABLE LAMINATE

The thermoformable laminate structure of this invention is useful in preparing molded thermoplastic foam articles.

5 Such molded thermoplastic foam articles are particularly useful when thermal or sound insulation is a desired property. The laminate provides three-dimensional rigidity over a wide temperature range.

10 This thermoformable laminate structure is particularly useful in preparing headliners for automobiles where the laminate provides for noise attenuation within the automobile. A particular useful headliner can be prepared by utilizing two sheets of laminate prepared according to this inven-
15 tion as covers for an inner core of a third polymeric foam, for instance a 250 mil (6.35 mm) thick, soft polyether, polyurethane foam. The three part composite can be prepared by using an adhesive on the bare surface of the laminate sheet to adhere to the soft,
20 foam core. The composite has the acrylic emulsion adhered fabric on its outer surfaces which allows for thermoformability of the composite. One surface of the composite can be covered with a vinyl covered, soft foam trim for an aesthetic interior surface.

25 While specific embodiments of the invention have been described, it should be apparent to those skilled in the art that various modifications thereof can be made without departing from the true spirit and scope of the invention. Accordingly, it is intended
30 that the scope of the following claims cover all such modifications which fall within the full inventive concept.

WE CLAIM:

1. A moisture-resistant, moldable, thermoformable laminate structure comprising:

(a) a sheet of a thermoplastic foam, said sheet having first and second surfaces; and

(b) a coating bonded to one of said surfaces; said coating being a polymer impregnated cloth; said polymer having a softening temperature greater than approximately 75°C.

2. The laminate of claim 1 wherein the polymer is an acrylic resin.

3. The laminate structure of claim 2 wherein the sheet of thermoplastic foam is selected from a group consisting of foamed polystyrene, foamed styrene-maleic anhydride polymer and foamed polyethylene.

4. The laminate structure of claim 1 wherein said cloth is a non-woven fabric.

5. The laminate structure of claim 2 wherein said acrylic polymer is styrene-methacrylic acid copolymer.

6. A process for forming a moldable thermoformable laminate structure having polymer impregnated cloth adhered to at least one side of a sheet of thermoplastic foam comprising

(a) applying a polymer emulsion film to a surface of a sheet of thermoplastic foam;

(b) allowing the emulsion film to dry by evaporation of emulsion liquids;

(c) applying a cloth to the dry emulsion film;

(d) impregnating the cloth with the polymer of the film by applying heat and

pressure to the surface of the cloth whereby the polymer becomes plastic and impregnates the cloth;

5 (e) and adhering the cloth to the sheet of film of plastic foam by removing said heat and pressure from the surface of the cloth, thereby allowing the polymer to cool and solidify.

10 7. The process of claim 6 wherein said sheet of thermoplastic foam comprises polystyrene or a copolymer of polystyrene or a copolymer of polystyrene.

15 8. The process of claim 7 wherein said polymer emulsion comprises an acrylic polymer having a softening temperature greater than 75°C.

9. The process of claim 8 wherein said emulsion film is applied to the sheet in an amount between 5 and 8 grams of liquid per square meter.

20 10. A process for providing a moldable, thermoformable laminate structure having polymer impregnated cloth adhered to at least one side of a sheet of thermoplastic foam comprising:

25 (a) applying a polymer emulsion film to a surface of a sheet of thermoplastic foam;

(b) applying a cloth to the emulsion film and allowing the polymer to impregnate the cloth; and

30 (c) adhering the cloth to the sheet by applying heat and pressure whereby the emulsion solids become plastic and removing the heat and pressure to allow the polymer to cool and solidify.

35 11. The process of claim 10 wherein the polymer emulsion film is allowed to dry prior to applying heat and pressure.

12. The process of claim 10 wherein the sheet of thermoplastic foam comprises polystyrene.

5 13. The process of claim 12 wherein the polymer emulsion film comprises an acrylic polymer emulsion wherein said polymer has a softening temperature greater than 75°C.

10 14. The process of claim 13 wherein the polymer emulsion film is applied to the surface of a sheet of thermoplastic foam at a level between 5 and 8 grams of liquid per square meter of thermoplastic foam.

15 15. A method of fabricating a moisture-resistant, moldable, thermoformable laminate structure comprising:

15 a) providing a sheet of thermoplastic foam having first and second surfaces;

20 b) impregnating a cloth with a polymer dissolved within a solvent, the polymer having a softening temperature greater than 75°C;

c) drying the polymer-impregnated cloth; and

25 d) bonding the polymer-impregnated cloth to the thermoplastic foam to form a laminate structure.

16. The method of claim 15 wherein the polymer-impregnated cloth is adhesively bonded to the first and second surfaces of the sheet of thermoplastic foam.



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(54) Thermoformable laminate structure.

(57) Thermoformable laminate structure comprising foamed thermoplastic sheet having a cloth adhesively bonded to one surface thereof. The cloth is impregnated with a polymer having a softening temperature greater than 75°C.

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EUROPEAN SEARCH REPORT

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	GB-A-1 149 305 (E.I. DU PONT DE NEMOURS & COMP.) * Claims 1-3,6,8-11,13-15; examples I,II,VI; page 2, lines 49-54, lines 69-72; page 3, lines 9-14, lines 27,28,41,46-80 *	1-4,15 ,16	B 32 B 5/24
A	---	5-14	
X	FR-A-1 298 431 (REGIE NAT. DES USINES RENAULT) * The whole document *	1-4	
A	---	5-16	
X	GB-A-1 467 766 (THE LUBRIZOL CORP.) * Figure 2; claims 1,3,4,8,9; page 1, lines 25-37,63-68,82-90; page 5, lines 50-113 *	1-4,15	TECHNICAL FIELDS SEARCHED (Int. Cl. 4) B 32 B
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A	GB-A-1 031 301 (FARBENFABRIKEN BAYER AKT.) * Figure 3; claims 1,8; page 1, line 64 - page 2, line 27; page 4, lines 83-95; page 10, lines 14-24 *	1-16	
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-03-1985	Examiner DE LA MORINERIE B.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
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X	--- GB-A-1 177 483 (THE DUNLOP COMP. LIM.) * Claims 1,3-5,8,18-20,25-27,32,33,35-37; page 1, lines 40-63; page 2, line 102 - page 3, line 95; page 4, lines 4-86; examples II,XI *	1-4,6- 8,10- 13,15- 16	
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X	--- FR-E- 95 925 (SCHOLL MANUF. COMP. LIM.) * Abstract 1-4; page 2, line 30 - page 3, line 15; page 4, lines 1-15; page 4, line 24 - page 6, line 2; page 6, line 6 - page 7, line 14; page 8, lines 14-27 * --- -/-	1,6,10	
The present search report has been drawn up for all claims			
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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A	FR-A-1 216 662 (SCHICKEDANZ) * Figures; abstract 1,2a,c; page 1, lines 24-35,43 - page 2, line 21; page 2, lines 79-83; page 2, line 95 - page 3, line 3 * -----	1-16	
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